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# Geochemical Controls on the Production and Distribution of Methylmercury in Near-Shore Marine Sediments

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We examined temporal differences in sedimentary production of monomethylmercury (MMHg) at three sites in Long Island Sound (LIS). Sediment-phase concentrations of Hg species decreased from west to east in LIS surface sediments, following the trend of organic matter. However, Hg methylation potentials, measured by incubation with an isotopic tracer ($^{200}$Hg), *increased* from west to east. $^{200}$Hg methylation potentials were enhanced in August relative to March and June, attributable to differences in activity of sulfate-reducing bacteria. Organic matter and acid-volatile sulfide influenced the distribution coefficient ($K_D$) of inorganic Hg (Hg(II) = total Hg − MMHg) and inhibited $^{200}$Hg methylation in surface sediments. $^{200}$Hg methylation varied inversely with the $K_D$ of Hg(II) and positively with the concentration of Hg(II), mostly as $HgS^0$, in LIS pore waters. Accordingly, we posit that a principal control on MMHg production in low-sulfide, coastal marine sediments is partitioning of Hg(II) between particle and dissolved phases, which regulates availability of Hg substrate to methylating bacteria. Most of the partitioning in LIS sediments is due to Hg−organic associations. This suggests that reductions in the organic content of coastal sediment, a potential result of nutrient abatement programs intended to inhibit eutrophication of near-shore waters, could enhance MMHg production by increasing the bioavailability of the large reservoir of "legacy Hg" buried within the sediment.

## Introduction

Monomethylmercury (MMHg) is the toxic form of Hg that can accumulate in fish to levels that may reduce the reproductive success of piscivorous wildlife (*1*) and the fish themselves (*2*) and pose a threat to human health (*3*). Humans are exposed to MMHg principally by consumption of fish and fish products (*4*), most (>60%) of which are from marine systems (*5*). Unfortunately, the biogeochemistry of Hg in near-shore and deep-water marine environs is understudied, with most research focused on terrestrial, freshwater, and atmospheric systems. Near-shore sediments are a repository for natural and pollution-derived Hg (*6*−*12*) and are a potentially significant source of MMHg to the marine food web, including fishes for human consumption. Indeed, many near-shore systems have accumulated large sedimentary burdens of anthropogenic Hg during the past 200 years, "legacy Hg" (*13*), and they host active communities of sulfate-reducing bacteria (SRB)—the principal group of organisms mediating transformation of inorganic Hg to MMHg (*14*, *15*).

Although sediments have long been recognized as a key location of microbial Hg methylation (*16*, *17*), only recently have some factors influencing sedimentary concentrations of MMHg been elucidated. Studies of MMHg levels in bulk surface sediment have shown dependencies on, for example, inorganic Hg, organic matter, and sulfide (*7*, *12*, *18*, *19*). It is unclear, however, if such variables affect the rate at which MMHg is produced (i.e., influencing Hg bioavailability and/or activity of methylating bacteria) or simply reflect the capacity of the sediment to retain MMHg. Recent mechanistic studies are addressing these issues. For example, Benoit et al. (*20*−*22*) demonstrated that sulfide influences MMHg production by controlling the chemical speciation and subsequent bioavailability of dissolved inorganic Hg to methylating bacteria.

We examined sedimentary production of MMHg in Long Island Sound (LIS), a large (3200 $km^2$) coastal embayment in the northeastern United States that supports a highly productive commercial and recreational fishery. LIS has been perturbed significantly by current and historic pollution, including sewage (*23*). As a consequence, it has longitudinal gradients in pollutant Hg, sediment geochemistry (e.g., organic matter, sulfide), and microbial and benthic infaunal activities that encompass ranges expected in most coastal regimes. Investigations across such sedimentary ranges can provide process/reaction-related information usually sought via laboratory experiments but under in situ conditions. Thus, LIS provides a useful setting to study biological and geochemical factors influencing MMHg production. We are investigating biogeochemical factors influencing rates of Hg methylation and MMHg concentrations in LIS sediments, specifically evaluating the roles of organic matter and sulfide. The results of this study are directly applicable to comparable environs and provide a biogeochemical framework for future study of MMHg production in other near-shore systems.

## Experimental Section

**Sediments.** Sediments were collected with a box corer from three sites in LIS (Figure 1) on August 15−16, 2001, March 12−14, 2002, and June 2, 2002. These sites span the sedimentary trophic gradient in LIS, which ranges from fine-grain, organic-rich substrate in the west to larger grain size (sandy), low-organic material in the east (*24*, *25*). Sampling periods reflect extremes in either sediment temperature (August and March) or delivery of autochthonous organic matter to LIS sediment. The June cruise was about 1 month after the spring phytoplankton bloom, typically observed in underlying sediment (i.e., chlorophyll *a*) about 2 weeks later (*26*). Water depths (m) at our sites are 18 (WLIS), 38 (CLIS), and 24 (ELIS). No benthic photosynthesis occurs at these sites; surface light is attenuated to <1% within the upper 5−15 m of LIS waters. Bottom water temperatures were similar (±1 °C) among sites within a given sampling period and averaged 20 °C in August, 5 °C in March, and 12 °C in June. Box-cored sediments and overlying water were subsampled with acid-cleaned polycarbonate tubes (inner diameter, 6.4 cm). Sediment cores for chemical analyses were stored in a refrigerator at 5−6 °C until sectioning, and those for the determination of $^{200}$Hg methylation rates were kept at bottom water temperature both prior to and during incubations in darkened flow-through containers on the deck of the research vessel.

Sediment cores for chemical analyses were sectioned within 18 h of collection and usually within 12 h. Cores were

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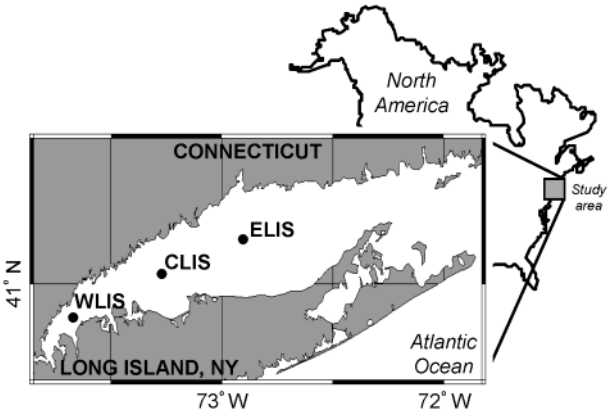


**FIGURE 1. Location of sediment sampling sites in Long Island Sound (WLIS, 40°55.10′ N, 73°38.57′ W; CLIS, 41°01.16′ N, 73°17.48′ W; ELIS, 41°06.10′ N, 72°56.04′ W).**

placed inside a low-oxygen (evacuated, $N_2$-filled) glovebox before overlying water was removed, and sediments were sectioned in 1-cm intervals downcore. Pore waters were extracted directly from August sediments by sequential vacuum filtration inside the glovebox, first through a glass fiber filter and then a 0.22-$\mu$m polycarbonate membrane filter. Pore waters were extracted from March and June sediments by centrifugation and vacuum filtration of the supernatant through 0.22-$\mu$m filters inside the glovebox (*27*). Acid-cleaned filters were rinsed with deoxygenated water immediately prior to sample filtration. Filtered pore water, containing both dissolved and colloidal Hg species, was acidified to about 0.5% final concentration with HCl (Trace Metal Grade) and stored frozen (−20 °C) until analysis. Sediment samples also were frozen immediately after removal from the glovebox.

**Hg Methylation Potentials.** Gross rates of Hg methylation were measured by adding trace quantities of isotopically enriched $^{200}Hg(NO_3)_2$ (Oak Ridge National Laboratory, 96.41% $^{200}Hg$) to two intact sediment cores from each site for each sampling period. This procedure is modeled after that employed for radiometric determinations with $^{203}Hg$ (*28, 29*), but it utilizes a stable isotope of Hg and detection by inductively coupled plasma mass spectrometry (ICPMS). A stock solution of $^{200}Hg$ (100 $\mu$g $Hg^{2+}$ $mL^{-1}$ in 5% $HNO_3$) was diluted with water overlying the sediments, and $^{200}Hg^{2+}$ was allowed to equilibrate with natural ligands for 1−2 h before 50 $\mu$L aliquots of the dilution were added to sediment cores in 1-cm vertical increments by injection through silicone septa. $^{200}Hg$ injections were dispersed throughout each sediment horizon to avoid localized concentration of added Hg in any one "injection channel." Added $^{200}Hg$ increased the ambient burden of sediment Hg by about 1%; a fraction much less than that added for determinations with $^{203}Hg$ or additions of natural Hg. Nevertheless, measured rates of $^{200}Hg$ methylation are considered *methylation potentials* as we assume that added $^{200}Hg$ has the same chemical speciation and sediment−water partitioning as ambient inorganic Hg. The calculated pH of $^{200}Hg$ dilutions ranged from 2.1 to 2.4; however, the small amount of acid transferred with $^{200}Hg$ to sediment (0.2−0.4 $\mu$eq $H^+$ per 32 $cm^3$ sediment) had a negligible effect on pore water pH. In laboratory tests with reconstituted sediment−water mixtures, no effect on pH was measured even when the $H^+$:sediment ratio (equivalents $H^+$:g of dry material) was 50-fold greater than that in $^{200}Hg$ incubation cores. Hence, the co-addition of small amounts of acid with $^{200}Hg$ to sediments for the methylation assays should have had no effect on the speciation of tracer Hg in incubation sediments. Sediment cores were incubated with added $^{200}Hg$ in the dark for about 4 h (August), 6 h (June), or 8 h (March) at the temperature of bottom water (±2 °C) before termination by sectioning and freezing of the sediment.

MMHg was extracted from incubated sediments with methods modified from Bloom and co-workers (*30*). Lyophilized sediment (2 g, ELIS; 1.3 g, CLIS and WLIS) was weighed accurately into 50-mL centrifuge tubes to which was added 3 mL of 20% (wt:vol.) KCl, 0.4 mL each of 9 M $H_2SO_4$ and 1 M $CuSO_4$, and 5 mL of $CH_2Cl_2$. Tubes were capped tightly, shaken vigorously by hand, and mixed on an orbital shaker for 2 h at 150 rpm to extract MMHg from the sediment into the organic phase, separating MMHg from inorganic Hg by solubility. Extraction tubes then were centrifuged at 2300 rpm for 15 min to separate particle, organic, and aqueous phases. Aliquots of organic phase were transferred to 15-mL centrifuge tubes (back-extraction tubes) containing 2.2 mL of reagent-grade water and 0.3 mL of BrCl solution (*31*). Care must be taken to not inadvertently transfer any of the aqueous phase when transferring the organic phase. Solutions in back-extraction tubes were shaken vigorously by hand and mixed on an orbital shaker for 1.5 h at 150 rpm; this step demethylates the MMHg and resulting inorganic Hg partitions into the aqueous phase. Aqueous and organic phases were separated by centrifugation for 3 min at 3000 rpm before 2 mL of the aqueous phase was transferred to an analysis tube containing 100 $\mu$L of 12 M HCl (Trace Metal Grade).

The amount of added $^{200}Hg$ transformed to methyl-$^{200}Hg$ during sediment incubation was measured by continuous-flow cold-vapor generation ICPMS, which utilizes an interfaced reaction chamber and membrane gas−liquid separator (GLS; *32*). Sample Hg was reduced to $Hg^0$ with 3% (wt:vol.) $SnCl_2$ in 1.5 M HCl inside a borosilicate glass reaction chamber and stripped from solution with Ar. $Hg^0$ from the reaction chamber was separated from aerosol droplets (and potential interferences) by passage through a PTFE-membrane GLS before introduction to the ICP torch. Hg isotope determinations were made with a Finnigan ELEMENT2 magnetic sector ICPMS. Calibrations of Hg isotope measurements were based on the atomic mass fraction of isotopes in certified Hg standards of natural isotopic abundance. Methylation of added $^{200}Hg$ was evaluated as the excess concentration of $^{200}Hg$ versus $^{198}Hg$ in sample extracts (*33*). The method detection limit (MDL) of these analyses is a function of ambient (background) MMHg concentration, natural abundance of $^{200}Hg$ (23.13%), and precision of our $^{198}Hg/^{200}Hg$ ratio measurements (*33*), which averaged 0.43% relative standard deviation (RSD) for a five independent extractions of a sediment (1.0 g of dry material each) containing 0.23 ng of MMHg $g^{-1}$dry weight. The amount of added $^{200}Hg$ that was methylated was greater than the MDL for all samples. The precision of $^{200}Hg$ methylation potential measurements averaged 16% RSD ($n = 21$), based on analyses of methodically replicated subsamples.

$^{200}Hg$ methylation potentials were corrected for "carry-over" of $Hg^{2+}$ into the $CH_2Cl_2$ phase during extraction. In natural waters and in our extraction procedure, $Hg^{2+}$ can form complexes that make it relatively hydrophobic (e.g., Hg−organic, $HgS^0$, $HgCl_2^0$) and consequently soluble in the $CH_2Cl_2$ phase of our initial extraction. Such carry-over Hg is interpreted as MMHg by our methodology, which assumes that all Hg partitioning into the $CH_2Cl_2$ phase is MMHg. We accounted for such potential transfer of $Hg^{2+}$ by adding either $^{201}Hg(NO_3)_2$ (Oak Ridge National Laboratory, 98.11% $^{201}Hg$) to incubated sediments before extraction (analysis by ICPMS) or $Hg^{2+}$ of natural abundance to similar extracts of LIS sediment and quantifying the carry-over by cold-vapor atomic fluorescence spectrometry (CVAFS).

Carry-over of added $Hg^{2+}$ from sediment into analytical extracts was assessed for the acid/$CH_2Cl_2$ extraction method. Lyophilized aliquots of selected incubated sediments (about 10% of total samples analyzed) were spiked with $^{201}Hg^{2+}$ to

about 1% of ambient Hg prior to extraction. The amount of $^{201}Hg$ added to dried sediment for evaluation of $Hg^{2+}$ carry-over was similar to the quantity of $^{200}Hg$ added to whole sediment prior to incubation for determination of methylation potential. Transfer of added $^{201}Hg^{2+}$ to analytical extracts of incubated sediment was evaluated as the excess concentration of $^{201}Hg$ versus $^{198}Hg$ (*33*). Carry-over of $^{201}Hg^{2+}$ in these sediments averaged 0.123% (1 SD, 0.033%; $n = 12$) of the nominal mass added prior to extraction. This fraction was similar to the amount of $Hg^{2+}$ carried over in samples where standard additions of natural abundance Hg were made to sediment prior to extraction and analysis with CVAFS (mean, 0.099%; 1 SD, 0.014%; $n = 6$). The "carry-over" of $Hg^{2+}$ observed in all of these tests, however, may be MMHg formed artifactually from the added Hg (*30*, *34*, *35*). Regardless of the mechanism by which added $^{201}Hg^{2+}$ or natural $Hg^{2+}$ resulted in the $CH_2Cl_2$ phase of our test extracts, we corrected the measured quantity of methyl-$^{200}Hg$ for 0.10% transfer of $^{200}Hg^{2+}$ added for the incubation assay.

In addition to added $Hg^{2+}$, ambient $Hg^{2+}$ also transferred from sediment into analytical extracts during the acid/$CH_2Cl_2$ extraction procedure. This was observed by comparing levels of total Hg in extracts of unspiked sediment (assumed to be 100% MMHg) with species-specific concentrations of MMHg in aqueous distillates (gas chromatographic CVAFS detection) of the same parent sediment. Levels of total Hg in acid/$CH_2Cl_2$ extracts, measured with both ICPMS and CVAFS, were 125−425% greater than those of aqueous distillates, indicating nonnegligible transfer of ambient $Hg^{2+}$ during the acid/$CH_2Cl_2$ extraction procedure. Carry-over of *ambient* $Hg^{2+}$, however, has no effect on our determination of $^{200}Hg$ methylation potentials, assuming that ambient Hg in LIS sediments has natural isotopic abundance and that individual isotopes are carried over in proportion to their atomic mass fraction. $^{200}Hg$ methylation potentials are based on recovery of excess $^{200}Hg$ versus $^{198}Hg$ from sample extracts. Positively biased recovery of bulk MMHg by the acid/$CH_2Cl_2$ extraction method also was evident from analyses of a sediment reference material (IAEA-405; International Atomic Energy Agency). Though biased in concentration by $Hg^{2+}$ carry-over, extraction of MMHg from sediment by the acid/$CH_2Cl_2$ method was quantitative; recovery of MMHg added to samples prior to acid/$CH_2Cl_2$ extraction averaged 95% (range, 80−122%).

**Sediment−Water Partitioning of Added $Hg^{2+}$.** A principal assumption of the $^{200}Hg$ methylation assay is that Hg added to sediment (i.e., $^{200}Hg^{2+}$) partitions between sediment and pore water phases in a manner similar to ambient $Hg^{2+}$. We examined the adsorption kinetics and steady-state partitioning of added Hg with sediments from each of the three study sites in the laboratory. Lyophilized sediment (0.5 g for ELIS; 0.3 g for CLIS and WLIS) was weighed accurately (±0.001 g) into 15-mL centrifuge tubes to which was added 10 mL of 0.22-$\mu$m filtered seawater from eastern LIS (salinity, 29.7‰; total Hg, 0.3 ng $L^{-1}$) and natural abundance $Hg^{2+}$. $Hg^{2+}$ additions enhanced the burden of ambient Hg 12- to 14-fold for each sediment. Duplicate sediment/water slurries were prepared for each sediment and reaction period (21 °C; 0.3, 5, 15, 45, 90, 360 min). Immediately after addition of $Hg^{2+}$, slurries were shaken vigorously by hand for 0.3 min and then agitated on an orbital shaker (100 rpm) for the remainder for the reaction period. Partitioning reactions were terminated by centrifugation of the samples at 3000 rpm for 3 min, followed immediately by filtration of the supernatant through an acid-cleaned 0.22-$\mu$m polycarbonate filter. Filtrates were digested with BrCl for 14−18 h before measurement of total Hg by CVAFS.

Added $Hg^{2+}$ readily adsorbs to LIS sediment particles, and its sediment−water partitioning is similar to that of ambient Hg. Our time-course assays showed that Hg adsorption to LIS sediment is rapid; more than 80% of added $Hg^{2+}$ was sequestered by the particle phase (i.e., >0.22 $\mu$m) within 0.3 min, and greater than 99% was adsorbed within 15 min. First-order rate constants for $Hg^{2+}$ adsorption to the sediments, estimated from the slurry experiments reacted for 0.3 min, ranged from 0.042 to 0.050 $s^{-1}$. Additionally, near steady-state partitioning of added $Hg^{2+}$ between particle and dissolved phases was achieved within 15−45 min, with the distribution coefficient ($K_D$; L $kg^{-1}$) of added $Hg^{2+}$ being similar to, or even slightly greater than, that for ambient Hg in both natural sediments and unspiked slurries. $K_D$ is calculated as the ratio of the concentration on the solid phase (sediment) to that in the enveloping aqueous phase. These experiments show the considerable Hg-binding capacity of ligands in natural sediments, even when organic content of the solid phase is low (1.9−7.8% loss-on-ignition).

A small amount of acid was transferred with $^{200}Hg$ to sediments for the methylation assays, and we tested the effect of such acid on Hg partitioning by adding $Hg^{2+}$ with and without the co-addition of $HNO_3$ to experimental sediment slurries. A no-acid $Hg^{2+}$ spiking solution was prepared by titrating an aliquot of the acidic $Hg^{2+}$ solution with KOH. Partitioning of Hg was similar between sediment samples spiked with acidic and no-acid aliquots of $Hg^{2+}$, even when the $H^+$:sediment ratio was about 100-fold greater than that of the $^{200}Hg$ methylation assays. Hence, the co-addition of small amounts of acid with $^{200}Hg$ to sediments for the methylation assays should have had no effect on sediment−water partitioning of the tracer.

**Hg Determinations by CVAFS.** Total Hg ($Hg_T$) and MMHg were measured in pore waters and lyophilized sediments. Sediment-phase $Hg_T$ and MMHg were defined procedurally as the fraction of each species remaining in sediment after removal of pore water. For $Hg_T$, we digested 0.1−0.3 g of lyophilized sediment with 5 mL of a 4:1 solution of 16 M $HNO_3$:12 M HCl in hermetically sealed Teflon bombs. Digestates were heated intermittently in a microwave oven for a total of 5 min, cooled to room temperature, and diluted with reagent-grade water, and 0.3 mL of BrCl solution was added. Filtered pore waters (4−10 mL) were digested with 0.2 mL each of BrCl solution and 16 M $HNO_3$ for about 24 h at room temperature. Hydroxylamine hydrochloride (12%, wt:vol.) was added as a prereductant to sediment and pore water digestates at least 1 h prior to analysis. Aliquots of digestates were added to reagent-grade water in a sparging flask followed by 0.1 mL of 50% (wt:vol.) $SnCl_2$ dissolved in 17% (vol.:vol.) HCl. $Hg^0$ was purged from solution with $N_2$ and quantified by dual gold-amalgamation CVAFS (*36*, *37*).

MMHg was extracted from filtered pore water and lyophilized sediment by aqueous distillation (*38*). Pore water (4−10 mL) and sediment (0.25−1.5 g) were added to 60-mL Teflon distillation vessels followed by additions of 30 mL of reagent-grade water, 0.2 mL of 20% (wt:vol.) KCl, and 0.4 mL of both 9 M $H_2SO_4$ and 1 M $CuSO_4$. Samples were distilled at 140 °C with $N_2$ purging until 60−80% of the sample solution was collected in similar 60-mL Teflon vessels immersed in an ice bath. MMHg in distillates was determined after aqueous-phase derivitization with sodium tetraethylborate, collection of volatile Hg species on Tenax, isothermal GC separation, pyrolytic decomposition of the ethylated species, and CVAFS detection (*39*). The difference between $Hg_T$ and MMHg in both sediment and pore water samples is defined as Hg(II). Thus, Hg(II) represents the sum of all $Hg^{2+}$ species that are complexed with inorganic and organic ligands.

**Geochemical Properties of Sediment.** We measured several geochemical properties of LIS sediment and assessed their relationships to Hg speciation and methylation. Dissolved sulfide ($S^{2-}$), oxygen, and pH were profiled electrochemically within 1 h of sediment collection (*40*). Dissolved oxygen at the sediment−water interface was similar to that

**TABLE 1. Mercury Speciation and Geochemical Properties of Surface Sediment (upper 4 cm) at the Three Sites in Long Island Sound in March 2002, June 2002, and August 2001[a]**

| site | period | sediment, ng $g^{-1}$ dry wt | | MMHg/ Hg(II) (%) | organic matter (% LOI) | AVS ($\mu$mol $kg^{-1}$) | pore water, ng $L^{-1}$ | | $^{200}$Hg potential (% $day^{-1}$)[b] | pore water Fe ($\mu$g $L^{-1}$)[c] | pH[c] | log $K_D$ (L $kg^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Hg(II) | MMHg | | | | Hg(II) | MMHg | | | | Hg(II) | MMHg |
| WLIS | March | 345 | 3.20 | 0.93 | 9.2 | 81 | 7.2 | 3.1 | 1.6 (0.1) | 400 | 7.38 | 4.69 | 3.01 |
| | June | 270 | 2.11 | 0.78 | 8.3 | 98 | 22.1 | 5.4 | 1.8 (0.1) | 1080 | 8.31 | 4.09 | 2.62 |
| | August | 325 | 2.51 | 0.77 | 8.6 | 168 | 5.6 | 4.6 | 2.9 (0.2) | | 7.39 | 4.76 | 2.74 |
| CLIS | March | 183 | 1.24 | 0.68 | 7.9 | 22 | 14.8 | 2.9 | 3.4 (0.3) | 380 | 7.50 | 4.09 | 2.63 |
| | June | 213 | 1.47 | 0.69 | 8.4 | 30 | 9.5 | 5.1 | 1.4 (0.2) | 1160 | 8.30 | 4.35 | 2.46 |
| | August | 251 | 1.46 | 0.58 | 8.3 | 24 | 12.3 | 3.0 | 4.6 (1.1) | | 7.45 | 4.31 | 2.69 |
| ELIS | March | 64 | 0.26 | 0.41 | 2.6 | 2 | 35.9 | 2.0 | 6.3 (0.5) | 1450 | 7.63 | 3.24 | 2.11 |
| | June | 39 | 0.41 | 1.05 | 2.2 | 3 | 11.6 | 6.1 | 4.0 (0.3) | 90 | 7.93 | 3.53 | 1.83 |
| | August | 43 | 0.20 | 0.47 | 2.2 | 6 | 16.1 | 3.3 | 8.2 (1.3) | | 7.14 | 3.43 | 1.78 |

[a] Dissolved sulfide was less than the detection limit (10 $\mu$M) in all surface sediments. [b] Values in parentheses are ±1 SE of the mean. [c] pH and pore water Fe values are the average of the upper 3 cm only. Fe was not measured in August.

in overlying water and penetrated no deeper than 0.6 cm in all sediment cores. Dissolved Fe (*41*) and acid-volatile sulfide (AVS) in fresh material (*42*), which includes free sulfides (i.e., $H_2S$, $HS^-$, $S^{2-}$) and FeS (*43*), were determined colorimetrically. Bulk organic content of sediments was measured gravimetrically as loss-on-ignition (LOI) of lyophilized material heated to 550 °C for at least 1 h (*44*).

**Quality Assurance of Hg Analyses.** Trace-metal clean procedures were employed throughout sample collection, processing, and analysis (*45, 46*). All equipment used for subsampling, sectioning, filtration, storage, and analysis of sediment and pore water was cleaned rigorously with acid and rinsed with reagent-grade water (nominal resistance, 18.2 MΩ $cm^{-1}$). Analyses of $Hg_T$ in sediment and pore water were calibrated with aliquots of $Hg^0$ taken from the headspace over pure liquid (*45*) and verified by comparison to analyses of aqueous standards prepared from a solution traceable to the National Institute of Standards and Technology (NIST). Recovery of aqueous Hg averaged 105% (95% CI, 102−108%) compared to $Hg^0$. MMHg in sediments and pore water was quantified after calibration with aliquots of a MMHg standard, which was prepared regularly from a 1000 mg $L^{-1}$ stock solution. Each MMHg standard was calibrated, after oxidation with BrCl, against $Hg^0$ and a NIST-traceable Hg solution.

The accuracy of our determinations of $Hg_T$ and MMHg for each analytical batch of samples was estimated by analyses of (1) procedural blanks taken through the digestion/distillation process, (2) certified reference materials MESS-2 (National Research Council of Canada) for $Hg_T$ and IAEA-405 (International Atomic Energy Agency) for MMHg, (3) replicate subsamples of sediment and pore water (method precision), (4) replicate analyses of the same subsample (analytical precision), and (5) spiked subsamples of sediment and pore water (MMHg only). Our mean measured concentration of $Hg_T$ in MESS-2 was 85 ng $g^{-1}$ dry weight, within the certified range of 82−100 ng $g^{-1}$. Recovery of MMHg from reference material IAEA-405 was biased high due to synthesis of artifact MMHg during distillation extraction (*35*). Previous work in our laboratory has demonstrated that little or no artifact MMHg is formed during distillation and analysis of LIS sediments (*35*). The mean recovery of spiked MMHg from distillates was 103% (95% CI, 99−106%). Analytical precision of $Hg_T$ measurements averaged 5.4% RSD ($n = 57$) and was similar to the method precision (mean, 4.6% RSD; $n = 13$). Analytical precision of MMHg determinations averaged 5.3% RSD ($n = 172$) and was slightly less than the method precision (mean, 7.3% RSD; $n = 64$). Estimated detection limits (ng $g^{-1}$ dry weight) for a 0.3-g sample were 0.4 for $Hg_T$ and 0.02 for MMHg. Detection limits for 5-mL aliquots of pore water were 0.2 ng $L^{-1}$ for MMHg and 1 ng $L^{-1}$ for $Hg_T$. Analyses of AVS and dissolved Fe were calibrated with standards prepared from reagent-grade chemicals. Method precision (RSD) of these measurements averaged 15% for both AVS ($n = 21$) and Fe ($n = 4$). The precision of procedurally replicated analyses of LOI averaged 3% RSD ($n = 81$).

## Results and Discussion

**Sediment-Phase Hg.** Concentrations of Hg species in surface sediment (average of upper 4 cm) at the three study sites are shown in Table 1. For surface sediment comparisons, we used the upper 4 cm of sediment because (1) it provides an integrated representation of bulk sediment collected by surface grabs, (2) it is a zone of greatest activity and diversity of bacteria and benthic infauna, and (3) the highest rates of MMHg production typically are observed in this region in freshwater (*15, 29, 47, 48*) and salt marsh sediments (*49*). Sediment-phase MMHg and Hg(II) were greatest at WLIS and decreased with eastward distance from New York City and the densely populated environs surrounding western LIS, following the trend of sedimentary organic matter. Mean levels of MMHg (ng $g^{-1}$ dry weight) in surface sediments were about 2.6 at WLIS, 1.4 at CLIS, and 0.3 at ELIS, within the range of those measured in other coastal marine sediments (*7, 9, 11, 12, 50, 51*). Hg(II) in surface sediment (ng $g^{-1}$ dry weight) was about 310 at WLIS, 220 at CLIS, and 50 at ELIS, with Hg(II) comprising roughly 99% of $Hg_T$; MMHg ranged 0.41−1.04% of $Hg_T$ in the sediment phase. Such levels of Hg(II) are representative of the typical range of sediment $Hg_T$ in LIS (*10*) and comparable to those in other urbanized near-shore systems (*7, 9, 12*) but less than those in nearby New York (*6*) and Boston (*8*) Harbors. Wastewater treatment facilities in the LIS watershed, the largest of which serve New York City and discharge into the East River, are a major source of Hg to the Sound (*10*). The west to east geographical trend of Hg(II) in LIS sediment reflects the impact of this and other modern/historical inputs of anthropogenic Hg to LIS.

**Organic Matter Controls Hg Distribution.** Organic matter is a major control on the distribution of $Hg_T$ in LIS sediments (Figure 2). The relationship in Figure 2, though limited in spatial coverage (i.e., no samples in 4−6% LOI range), is robust as it includes samples from all collection periods, sites, and sediment to depths of 10 cm ($n = 110$). It clearly portrays the significance of organic−Hg associations in the Sound and its sediments. The affinity of organic matter for Hg(II) is well established, both in coastal waters (*52*−*54*) and sediments (*10, 12, 55*). MMHg was not related as strongly with organic matter in the same samples ($r^2 = 0.56$); however, MMHg followed organic content more closely when only the upper 4 cm of sediment was considered ($r^2 = 0.73$).

**$^{200}$Hg Methylation Potentials.** In contrast to decreasing concentrations of Hg species, $^{200}$Hg methylation potentials increased from west to east in LIS surface sediment, and this

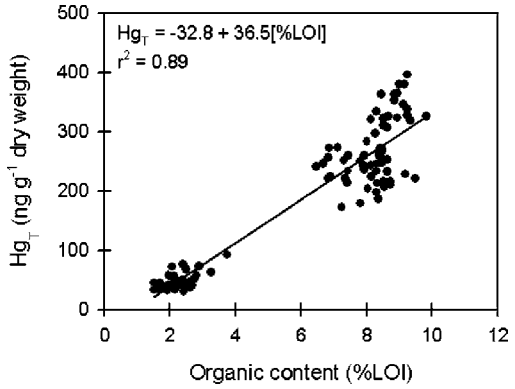


**FIGURE 2. Relation between total Hg ($Hg_T$) and organic content of sediments from all sampling periods, sites, and depths in LIS.**

trend was consistent for all sampling periods (Table 1). $^{200}$Hg methylation increased from 1.6% day$^{-1}$ at WLIS to 6.3% day$^{-1}$ at ELIS in March, from <2% day$^{-1}$ at CLIS and WLIS to 4.0% day$^{-1}$ at ELIS in June, and from 2.9% day$^{-1}$ at WLIS to 8.2% day$^{-1}$ at ELIS in August. Such a geographical pattern is contrary to what would be expected if SRB activity alone were controlling Hg methylation. The activity of SRB in coastal marine sediments is limited by organic matter (*56*, *57*), and the CLIS and WLIS sediments have considerably more organic matter than ELIS. In addition, the CLIS and WLIS sediments have greater amounts of AVS than ELIS. AVS may be interpreted as a proxy for the relative activity of SRB (*58*, *59*), assuming that AVS is oxidized similarly among sites.

Hg methylation also varied temporally in surface sediments of LIS (Table 1). Among sampling periods, $^{200}$Hg methylation in surface sediment was greater in August than in June or March. Physicochemical properties of the environment can affect Hg methylation by influencing either the activity of methylating bacteria or the bioavailability of Hg(II) substrate. Given that the geographical trend in $^{200}$Hg methylation was consistent temporally, although the magnitude of methylation varied among sampling periods, it is reasonable to infer that the seasonal variation of $^{200}$Hg methylation in LIS sediments was due to a common factor. We argue that the observed temporal differences in Hg methylation were due principally to the effect of temperature on microbial activity.

Temperature affects both SRB activity (*60*) and Hg methylation (*47*, *48*, *61*). Greater $^{200}$Hg methylation potentials were expected in August as the temperature of bottom water (i.e., surface sediment) was highest during this sampling period. However, we did not expect that $^{200}$Hg methylation in June (12 °C) would be equal to or less than that in March (5 °C). The June collections occurred after the spring phytoplankton bloom in LIS, which results in a considerable flux of labile organic matter to the sediment (*26*). This flux and the increased temperatures should enhance bacterial activity in the June sediments; however, Hg methylation did not increase. This apparent anomaly may be due to microorganisms other than SRB dominating the sedimentary microbial community of LIS in June. We observed that pore water pH was markedly greater in June than in March or August at all sites and that pore water Fe was greater in June than in March at CLIS and WLIS (Table 1). Dissimilatory iron-reducing bacteria (DIRB) can utilize $Fe^{3+}$ in solid Fe oxyhydroxides (e.g., $Fe(OH)_3$, FeOOH, $Fe_2O_3$) as an electron acceptor (*62*−*64*). Such reactions liberate $Fe^{2+}$ from the mineral phase and consume protons (*64*), thereby increasing pore water pH. Changes in pore water Fe and pH from March to June at WLIS and CLIS are consistent with the 3:1 $OH^-$:$Fe^{2+}$ stoichiometry of DIRB-mediated dissolution of Fe oxyhydroxides. If the activity of DIRB were enhanced in June,

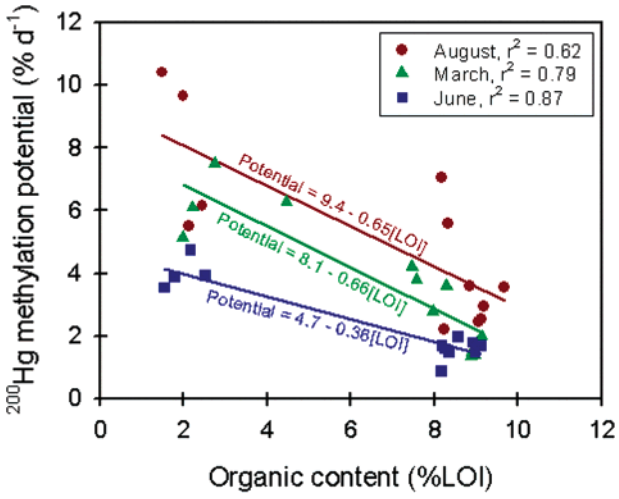


**FIGURE 3. Relation between $^{200}$Hg methylation and organic content of surface sediments in LIS.**

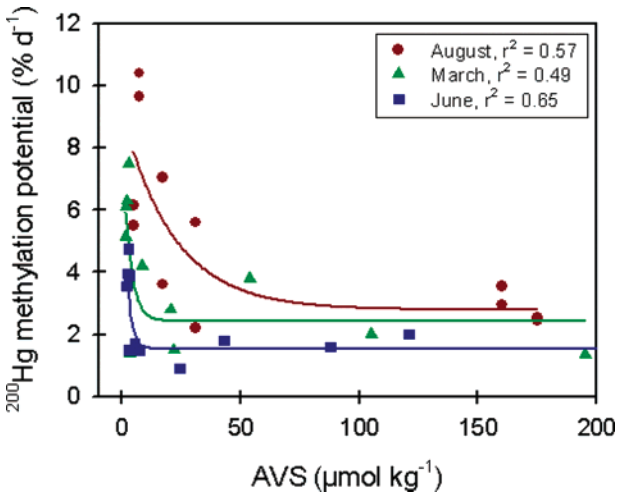


**FIGURE 4. Relation between $^{200}$Hg methylation and acid-volatile sulfide (AVS) in surface sediments of LIS. Regressions were modeled with a three-parameter exponential decay function ($y = y_0 + ae^{-bx}$).**

then they could have inhibited SRB-mediated Hg methylation through several potential mechanisms. These mechanisms include (1) competition of DIRB with SRB for carbon and energy sources, (2) reduction of Hg(II) availability by enhancing pore water $Fe^{2+}$ (*65*), and (3) inhibition of facilitated uptake of Hg(II) by increasing pH (*66*). Furthermore, if DIRB did dominate the microbial community in June, then they do not appear to be as effective methylators of Hg as SRB, which typically proliferate in anoxic marine sediments (*67*).

**Geochemical Controls on Hg Methylation.** Organic matter and AVS inhibit Hg methylation in surface sediments of LIS. $^{200}$Hg methylation was related inversely with organic matter during all sampling periods (Figure 3). Regression lines for the August and March samples vary only in *y*-intercept, whereas both the slope and *y*-intercept of the June samples are considerably less than the other two periods. These results show that the inhibitory effect of organic matter is proportional to its concentration and suggest that other factors (e.g., microbial activity) influence the magnitude (*y*-intercept) of Hg methylation temporally. $^{200}$Hg methylation in surface sediments also was constrained by AVS, especially at the lower concentrations (Figure 4). Indeed, Hg methylation was reduced markedly by AVS as low as 10−30 μmol kg$^{-1}$, with higher concentrations having little greater effect. We suggest that the inhibitory effects of both organic matter

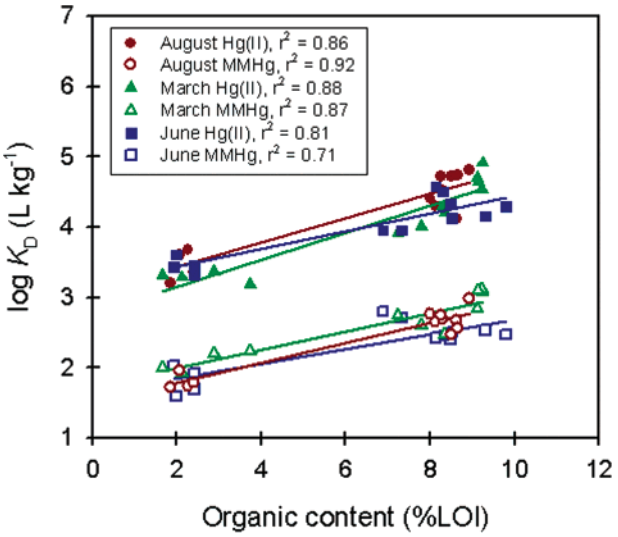


**FIGURE 5. Relation between the distribution coefficient ($K_D$) of Hg species and organic content of surface sediments in LIS.**

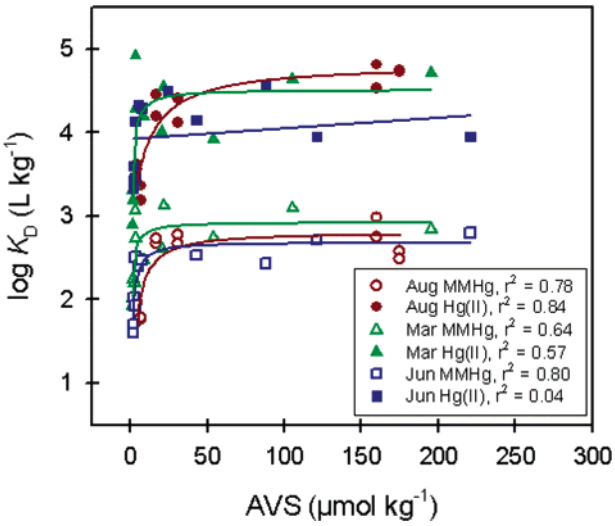


**FIGURE 6. Relation between the distribution coefficient ($K_D$) of Hg species and acid-volatile sulfide (AVS) in surface sediments of LIS. Regressions were modeled with a three-parameter hyperbolic function ($y = y_0 + axl[b + x]$).**

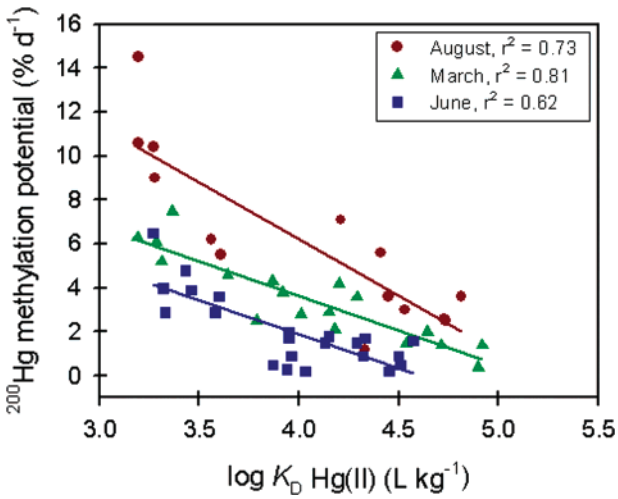


**FIGURE 7. Relation between $^{200}$Hg methylation and the distribution coefficient ($K_D$) of Hg(II) in sediments of LIS.**

and AVS on $^{200}$Hg methylation result from their influence, possibly in concert, on the partitioning and subsequent availability of pore water Hg(II) to methylating bacteria.

Figure 5 shows the positive relationship between log $K_D$ of both MMHg and Hg(II) versus quantity of organic matter in surface sediments from each sampling period. log $K_D$ of Hg(II) ranged 3.18−4.92 and averaged 4.06 in surface sediments. MMHg was less strongly associated with the sediment phase, having a mean log $K_D$ of 2.43 (range, 1.59−3.12). These values are about 6- and 2-fold less than those measured for Hg(II) and MMHg in sediments of Lavaca Bay, TX (*9*), the only other marine system known to have reported $K_D$ values for both MMHg and Hg(II) in sediment. Preferential adsorption of Hg species to sediment particles with increasing organic concentration was temporally consistent as there was little variation among sampling periods. These results suggest that the adsorptive affinity of organic matter for both Hg species in surface sediments of LIS is similar among sites and sampling periods and that sediment−water partitioning of both Hg(II) and MMHg is controlled dominantly by the amount of organic matter. The small differences in salinity among sites and sampling periods (range in overlying water, 26.9−30.6‰) would have limited influence on the observed sediment−water partitioning of Hg species in LIS (*53*).

Sediment−water partitioning of Hg is well described by organic content; however, AVS may impart some control on the $K_D$ of Hg(II) and MMHg (Figure 6). The effect of AVS on $K_D$ of both species in surface sediment is best represented by hyperbolic functions. The $K_D$ of Hg(II) increased about $10^{1.5}$ over the 0−20 $\mu$mol kg$^{-1}$ range in AVS and did not change with greater concentrations. A similar trend was observed for MMHg, with the $K_D$ increasing about 10-fold over the same narrow range in AVS.

Organic matter is a covariate in the relation between the $K_D$ of Hg species and AVS (Figure 6); this is similar to the relation between $^{200}$Hg methylation and AVS (Figure 4). Surface sediments from the ELIS site had relatively low levels of both AVS and organic matter, whereas those at WLIS had greater concentrations of each. The CLIS sediments, however, allow discrimination between the relative roles of organic matter and AVS in affecting the $K_D$; they have an organic content comparable to WLIS sediments but low AVS (Table 1). The CLIS samples are situated at the inflection of the hyperbolas in Figure 6 and have $K_D$ values similar to those of the WLIS samples, although their AVS levels are much less. Thus, the observed effects of AVS on $^{200}$Hg methylation and $K_D$ of Hg species may simply be an artifact of covariation with organic matter in LIS. We are examining the relative roles of AVS and organic matter in affecting Hg methylation and sediment−water partitioning in New York/New Jersey Harbor with a more diverse and contrasting range of these constituents. Preliminary results show that the $K_D$ of MMHg is related linearly with organic matter (similar to LIS sediments) and unrelated to AVS.

**Methylation of Dissolved Hg(II).** Hg methylation in LIS sediments is controlled by availability of dissolved Hg(II) to methylating bacteria. $^{200}$Hg methylation was related inversely with the $K_D$ of Hg(II) (Figure 7), meaning that Hg methylation is greater in sediments where proportionately more of the ambient Hg(II) is in pore water. Thus, sediments with less organic matter (e.g., ELIS) have proportionately more Hg(II) in the dissolved phase (i.e., lower $K_D$) and $^{200}$Hg methylation is enhanced. It is clear from Figure 7 that the magnitude of $^{200}$Hg methylation varied temporally, although inverse relations were observed for each sampling period. We attribute the temporal differences to seasonal fluctuations in the activity of SRB.

Our investigation indicates that a principal constraint on Hg methylation in low-sulfide, near-shore marine sediments is partitioning of Hg(II) between pore water and particle phases, which is governed by geochemical characteristics of

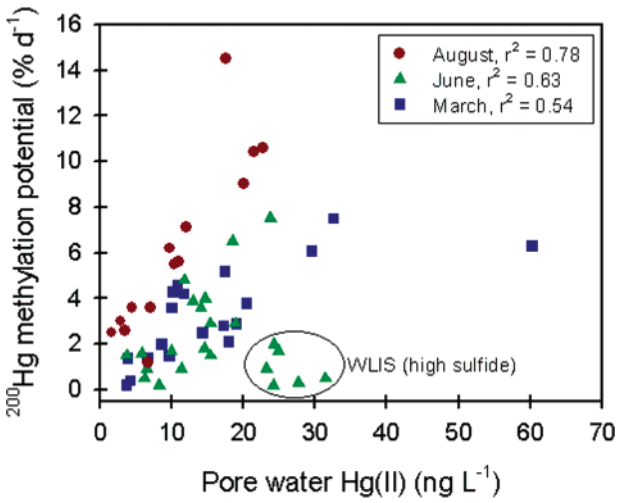


**FIGURE 8. Relation between $^{200}$Hg methylation and Hg(II) in pore water of LIS sediments. Circled samples were not included in the June regression analysis.**

the sediment. If $^{200}$Hg methylation is related to partitioning of Hg(II) and Hg(II) must be dissolved to be methylated microbially (*21*), then there should be a relationship between $^{200}$Hg methylation and Hg(II) in pore water of LIS sediments. Figure 8 shows that nearly all of the data points (excluding those circled; see below) are within a relatively narrow range. Samples from August comprise the upper limit of this relationship, and those from March and June are the lower boundary. This coherence establishes the availability of dissolved Hg(II) to methylating bacteria as a major factor determining MMHg production in near-shore sediments. It also demonstrates a range in Hg methylation potentials that can be attributed to activity of SRB (*68*, *69*).

Hg methylation in *sulfidic* sediment pore waters is not related to the supply of dissolved Hg(II) but rather a particular species of Hg(II), $HgS^0$ (*22*). Hg(II) must enter the bacterial cell to be methylated, most likely by passive diffusion through the cell membrane as a dissolved, neutrally charged complex (*21*, *22*), which is $HgS^0$ in pore water (*20*). MMHg production in pure cultures of sulfate-reducer *Desulfobulbus propionicus* (*1pr3*) was correlated strongly with calculated concentrations of $HgS^0$ but only weakly related to total dissolved Hg(II) (*22*). Empirically, we found that methylation of Hg(II) in sediments of LIS was related simply to its partitioning from the solid phase and the concentration of dissolved Hg(II), having undetermined complexation.

Our findings are, however, reconcilable with those of Benoit et al. (*22*). We infer from their chemical speciation model (*20*) that in most sediments of LIS, where dissolved sulfide was less than about 10 $\mu$M (detection limit), $HgS^0$ was the dominant complex of dissolved Hg(II), meaning that most of the Hg(II) in LIS pore waters was biologically available for methylation. Dissolved sulfide does not accumulate to considerable levels in surface sediments of coastal marine systems as a result of pore water irrigation by benthic infauna (*58*) and relatively high levels of dissolved Fe (*59*, *70*, *71*). Shown circled in Figure 8 are samples from the 4−10 cm depth horizons at WLIS. These samples stand apart from the others, having much lower $^{200}$Hg methylation than expected based on their Hg(II) concentrations and having greater levels of dissolved sulfide (50−200 $\mu$M). Such levels of sulfide would mean that $HgHS_2^-$ was the major Hg−S complex in these pore waters (*20*). Inhibited $^{200}$Hg methylation in these sediments can be attributed to $HgHS_2^-$ being much less bioavailable to methylating bacteria than $HgS^0$ (*21*, *22*), the inferred dominant complex in all other LIS samples.

**MMHg Accumulation and $^{200}$Hg Methylation.** MMHg was positively related to Hg(II) in surficial sediments of LIS (Figure 9). Although MMHg:Hg(II) concentration ratios of individual samples or groups of samples (Table 1) deviate slightly from the system-wide mean of 0.83% (slope of regression), the trend of increasing sediment MMHg with Hg(II) is significant ($r^2 = 0.88$, $p < 0.0001$) and the *y*-intercept does not differ from zero ($p = 0.18$). This relationship is striking because the samples were collected during different seasons and from sites that contrasted considerably in geochemical composition and $^{200}$Hg methylation potentials of microbial populations (Table 1). In a recent review, Benoit et al. (*19*) showed that ambient levels of MMHg are often correlated with short-term rates of isotope Hg methylation in organic-rich freshwater sediments, though tracer incubations frequently overestimate methylation of ambient inorganic Hg. In surface sediments of LIS, however, accumulation of MMHg normalized to Hg(II) (i.e., MMHg:Hg(II) concentration ratio) was relatively similar throughout the Sound (i.e., Figure 9) and unrelated, if not inversely related, to $^{200}$Hg methylation potential ($r = -0.36$, $p = 0.03$). Several explanations for the lack of positive agreement between MMHg accumulation and gross $^{200}$Hg methylation potential in LIS are possible, including (1) the chemical speciation and sediment−water partitioning of added $^{200}$Hg did not reflect that of ambient $Hg^{2+}$ and (2) some, if not much, of the MMHg produced in the sediments of LIS is not accumulated in the solid phase and is lost to other sinks (e.g., bacterial demethylation, diffusion/advection to overlying water, bioaccumulation). To the best of our knowledge and efforts, $^{200}$Hg added to sediment for methylation assays had both the same sediment−water partitioning and chemical speciation as ambient $Hg^{2+}$; thus, the disconnection between $^{200}$Hg methylation and MMHg accumulation in LIS sediments may be loss of MMHg produced therein.

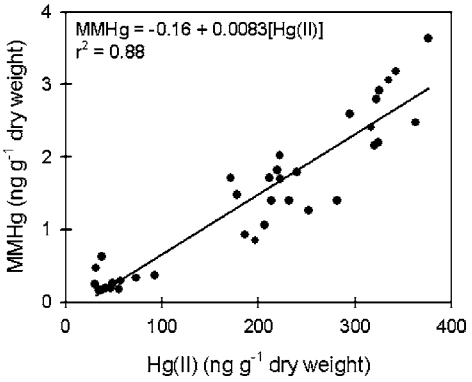


**FIGURE 9. Relation between MMHg and Hg(II) in surficial sediments (upper four cm) of LIS from all sampling periods and sites.**

The loss of MMHg from LIS surface sediments is large in comparison to the amount accumulated. While we did not assess MMHg demethylation or bioaccumulation in surface sediment, we estimated that the diffusional flux of dissolved MMHg from LIS sediment is $11 \pm 4$ kg year$^{-1}$ (*72*). This loss is considerably greater than the estimated accumulation of MMHg in surface sediment of LIS (1 kg year$^{-1}$), which is based on mean sediment values of 140 ng g$^{-1}$ dry weight for $Hg_T$ (*10*), 0.008 for sediment-phase MMHg:$Hg_T$, and an average sediment accumulation rate of 0.03 g cm$^{-2}$ year$^{-1}$ for the whole basin. The sedimentation rate was calculated by dividing the estimated mass of fine-grained material supplied to LIS ($9.3 \times 10^8$ kg year$^{-1}$; *24*) by the total area ($3.2 \times 10^9$ m$^2$). Hence, compared to diffusional losses alone, much of the MMHg produced in surface sediment of LIS is not accumulated by the solid phase, and we should not expect MMHg:Hg(II) ratios to reflect $^{200}$Hg methylation potentials in this system.

**Controls on Sediment MMHg Accumulation.** With regard to widely varying $^{200}$Hg methylation and potentially significant

losses of MMHg to diffusion/advection/bioaccumulation, why are sediment-phase concentrations of MMHg and Hg(II) almost constantly proportional in surface sediments of LIS (Figure 9)? One explanation for similar MMHg:Hg(II) concentration ratios is that sediment−water partitioning of both Hg species is controlled by the same physicochemical properties of the sediment. Accordingly, the concentration ratio of MMHg:Hg(II) in the sediment phase represents a steady-state condition governed by the affinity of the sediment for each species. The fraction of $Hg_T$ as MMHg in coastal marine sediment typically ranges from 0.002 to 0.02 (*7*, *9*, *12*, *51*). Likewise, estimated MMHg:Hg(II) $K_D$ ratios often range from 0.005 to 0.05 in near-shore surface sediments (Table 1 of this study; *9*). If partitioning of Hg in sediments is at steady-state, then $K_D$ values estimated from in situ concentrations are indicative of the ratio of first-order rate constants for adsorption and desorption reactions with the solid phase (i.e., $k_{adsorption}$:$k_{desorption}$). Therefore, the similarity between MMHg:Hg(II) concentration ratios and MMHg:Hg(II) $K_D$ ratios in marine sediments may be the result of proportional sediment−water partitioning and retention of the Hg species, which is influenced by geochemical characteristics of the solid phase (e.g., organic content). Such a geochemical control could explain the relatively constant MMHg:Hg(II) concentration ratio observed in LIS.

## Summary

This work demonstrates that both geochemical and microbial elements interrelate to influence rates of Hg methylation and MMHg concentrations in near-shore marine sediments. We found that potential rates of microbial Hg methylation are related inversely with sedimentary organic content, which governs the partitioning of Hg(II) between dissolved and sediment phases. Such partitioning is the principal control on MMHg production in low-sulfide LIS sediments; Hg methylation was related inversely with the $K_D$ of Hg(II) and positively related to the concentration of Hg(II) in pore water. Additionally, differences in Hg methylation were observed among seasonal sampling periods, illustrating the role of methylating bacteria (SRB) in utilizing available substrate Hg(II). Accumulation of MMHg in surface sediments of LIS, however, is not directly related to potential rates of bacterial Hg methylation; much of the MMHg produced in sediments is lost to overlying water. Concentrations of MMHg and Hg(II) in surface material are relatively proportional throughout LIS and influenced by the adsorptive affinity of the solid phase for each Hg species, which is affected principally by sedimentary organic content.

Our results suggest that MMHg production is Hg-limited in LIS sediments and by extension other near-shore regimes. Hg methylation in LIS is controlled by sediment−water partitioning of Hg(II), which is influenced largely by the organic content of the solid phase. Reducing the organic content of sediment, therefore, could increase pore water Hg(II) and enhance bacterial production of MMHg. Management programs intended to minimize anthropogenic nutrient loading to coastal systems, in an attempt to curb eutrophication and hypoxia/anoxia in the water column, may inadvertently enhance production of MMHg in underlying sediments by reducing the supply of autochthonous material. Such a reduction in organic delivery would not, however, significantly affect the methylating potential of benthic microbial communities; the greatest Hg methylation potentials in LIS were measured in sediments having about 2% organic content. A lowered organic content of sediment also may lessen the affinity of particles for adsorption and retention of toxic MMHg produced therein, meaning more MMHg is mobilized to overlying water. Furthermore, the large reservoir of "legacy Hg" buried within the sediment may become more reactive biologically as the activity of burrowing infauna increases with improving water conditions. Bioturbation can redistribute "legacy Hg" within the sedimentary column to zones of active biological methylation, creating the potential for methylation, mobilization, and bioaccumulation of pollutant Hg that was buried during the past 200 years.

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## Literature Cited

(1) Wiener, J. G.; Krabbenhoft, D. P.; Heinz, G. H.; Scheuhammer, A. M. In *Handbook of Ecotoxicology*; Hoffman, D. J., Rattner, B. A., Burton, G. A., Jr., Cairns, J., Jr., Eds.; Lewis Publishers: Boca Raton, FL, 2002; pp 409−463.

(2) Hammerschmidt, C. R.; Sandheinrich, M. B.; Wiener, J. G.; Rada, R. G. *Environ. Sci. Technol.* **2002**, *36*, 877−883.

(3) Grandjean, P.; Weihe, P.; White, R. F.; Debes, F.; Araki, S.; Yokoyama, K.; Murata, K.; Sorenson, N.; Dahl, R.; Jorgensen, P. *Neurotoxicol. Teratol.* **1997**, *19*, 417−428.

(4) Fitzgerald, W. F.; Clarkson, T. W. *Environ. Health Perspect.* **1991**, *96*, 159−166.

(5) U.S. Environmental Protection Agency. EPA-821-C-02-003; U.S. Environmental Agency: Washington D.C., 2002.

(6) Adams, D. A.; O'Connor, J. S.; Weisberg, S. B. U.S. EPA/902-R-98-001; U.S. Environmental Protection Agency: Edison, NJ, 1998.

(7) Mason, R. P.; Lawrence, A. L. *Environ. Toxicol. Chem.* **1999**, *18*, 2438−2447.

(8) Bothner, M. H.; Buchholtz ten Brink, M.; Manheim, F. T. *Mar. Environ. Res.* **1998**, *45*, 127−145.

(9) Bloom, N. S.; Gill, G. A.; Cappellino, S.; Dobbs, C.; McShea, L.; Driscoll, C.; Mason, R.; Rudd, J. *Environ. Sci. Technol.* **1999**, *33*, 7−13.

(10) Varekamp, J. C.; Buchholtz ten Brink, M. R.; Mecray, E. L.; Kreulen, B. *J. Coast. Res.* **2000**, *16*, 613−626.

(11) Covelli, S.; Faganeli, J.; Horvat, M.; Brambati, A. *Appl. Geochem.* **2001**, *16*, 541−558.

(12) Conaway, C. H.; Squire, S.; Mason, R. P.; Flegal, A. R. *Mar. Chem.* **2003**, *80*, 199−225.

(13) Fitzgerald, W. F.; Lamborg, C. H. In *Treatise on Geochemistry*; Sherwood-Lollar, B., Ed.; Elsevier: New York; **2003**, *9*, 107−148.

(14) Compeau, G.; Bartha, R. *Appl. Environ. Microbiol.* **1985**, *50*, 498−502.

(15) Gilmour, C. C.; Henry, E. A.; Mitchell, R. *Environ. Sci. Technol.* **1992**, *26*, 2281−2288.

(16) Jensen, S.; Jernelöv, A. *Nature* **1969**, *223*, 753−754.

(17) Olson, B. H.; Cooper, R. C. *Water Res.* **1976**, *10*, 113−116.

(18) Krabbenhoft, D. P.; Wiener, J. G.; Brumbaugh, W. G.; Olson, M. L.; DeWild, J. F.; Sabin, T. J. In *U.S. Geological Survey Toxic Substances Hydrology Program−Proceedings of the Technical Meeting, Vol. 2, Contamination of Hydrologic Systems and Related Ecosystems*; Morganwalp, D. W., Buxton, H. T., Eds.; U.S. Geological Survey Water Resources Investigation Report 99-4018B; U.S. Geological Survey: Denver, 1999; Vol. 2, pp 147−160.

(19) Benoit, J. M.; Gilmour, C. C.; Heyes, A.; Mason, R. P.; Miller, C. L. In *Biogeochemistry of Environmentally Important Trace Elements*; Cai, Y., Braids, O. C., Eds.; American Chemical Society: Washington, D.C., 2003; pp 262−297.

(20) Benoit, J. M.; Gilmour, C. C.; Mason, R. P.; Heyes, A. *Environ. Sci. Technol.* **1999**, *33*, 951−957.
(21) Benoit, J. M.; Mason, R. P.; Gilmour, C. C. *Environ. Toxicol. Chem.* **1999**, *18*, 2138−2141.
(22) Benoit, J. M.; Gilmour, C. C.; Mason, R. P. *Environ. Sci. Technol.* **2001**, *35*, 127−132.
(23) Buchholtz ten Brink, M. R.; Mecray, E. L.; Galvin, E. L. *J. Coast. Res.* **2002**, *16*, 591−612.
(24) Knebel, H. J.; Poppe, L. J. *J. Coast. Res.* **2000**, *16*, 533−550.
(25) Poppe, L. J.; Knebel, H. J.; Mlodzinska, Z. J.; Hastings, M. E.; Seekins, B. A. *J. Coast. Res.* **2000**, *16*, 567−574.
(26) Gerino, M.; Aller, R. C.; Lee, C.; Cochran, J. K.; Aller, J. Y.; Green, M. A.; Hirschberg, D. *Estuar. Coast. Shelf Sci.* **1998**, *46*, 531−547.
(27) Mason, R.; Bloom, N. S.; Cappellino, S.; Gill., G.; Benoit, J.; Dobbs, C. *Environ. Sci. Technol.* **1998**, *32*, 4031−4040.
(28) Gilmour, C. C.; Riedel, G. S. *Water Air Soil Pollut.* **1995**, *80*, 747−756.
(29) Gilmour, C. C.; Riedel, G. S.; Ederlington, M. C.; Bell, J. T.; Benoit, J. M.; Gill, G. A.; Stordal, M. C. *Biogeochemistry* **1998**, *40*, 327−345.
(30) Bloom, N. S.; Colman, J. A.; Barber, L. *Fresenius J. Anal. Chem.* **1997**, *358*, 371−377.
(31) Bloom, N. S.; Crecelius, E. A. *Mar. Chem.* **1983**, *14*, 49−59.
(32) Klaue, B., Blum, J. D. *Anal. Chem.* **1999**, *71*, 1408−1414.
(33) Hintelmann, H.; Evans, R. D. *Fresenius J. Anal. Chem.* **1997**, *358*, 378−385.
(34) Hintelmann, H.; Falter, R.; Ilgen, G.; Evans, R. D. *Fresenius J. Anal. Chem.* **1997**, *358*, 363−370.
(35) Hammerschmidt, C. R.; Fitzgerald, W. F. *Anal. Chem.* **2001**, *73*, 5930−5936.
(36) Fitzgerald, W. F.; Gill, G. A. *Anal. Chem.* **1979**, *51*, 1714−1720.
(37) Bloom, N. S.; Fitzgerald, W. F. *Anal. Chim. Acta* **1988**, *208*, 151−161.
(38) Horvat, M.; Bloom, N. S.; Liang, L. *Anal. Chim. Acta* **1993**, *281*, 135−152.
(39) Bloom, N. S. *Can J. Fish. Aquat. Sci.* **1989**, *46*, 1131−1140.
(40) Visscher, P. T.; Beukema, J.; Van Gemerden, H. *Limnol. Oceanogr.* **1992**, *36*, 1476−1480.
(41) American Public Health Association, American Water Works Association, and Water Environment Federation. *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; American Public Health Association: Washington, D.C., 1995.
(42) Trüper, H. G.; Schlegel, H. G. *J. Microb. Serol.* **1964**, *30*, 225−238.
(43) Fossing, H.; Jørgensen, B. B. *Biogeochemistry* **1989**, *8*, 205−222.
(44) Heiri, O.; Lotter, A. F.; Lemcke, G. *J. Paleolimnol.* **2001**, *25*, 101−110.
(45) Gill, G. A.; Fitzgerald, W. F. *Mar. Chem.* **1987**, *20*, 227−243.
(46) Fitzgerald, W. F. In *Clean Hands: Patterson's Crusade Against Lead Contamination in the Environment*; Davidson, C., Ed.; Nova Science Publishers: Commack, NY, 1999; pp 119−137.
(47) Korthals, E. T.; Winfrey, M. R. *Appl. Environ. Microbiol.* **1987**, *53*, 2397−2404.
(48) Winfrey, M. R.; Rudd., J. W. M. *Environ. Toxicol. Chem.* **1990**, *9*, 853−869.
(49) Langer, C. S.; Fitzgerald, W. F.; Visscher, P. T.; Vandal, G. M. *Wetl. Ecol. Managem.* **2001**, *9*, 295−310.
(50) Gagnon, C.; Pelletier, É.; Mucci, A.; Fitzgerald, W. F. *Limnol. Oceanogr.* **1996**, *41*, 428−434.
(51) Mikac, N.; Niessen, S.; Ouddane, B.; Wartel, M. *Appl. Organomet. Chem.* **1997**, *13*, 715−725.
(52) Coquery, M.; Cossa, D.; Sanjuan, J. *Mar. Chem.* **1997**, *58*, 213−227.
(53) Turner, A.; Millward, G. E.; Le Roux, S. M. *Environ. Sci. Technol.* **2001**, *35*, 4648−4654.
(54) Lamborg, C. H.; Fitzgerald, W. F.; Skoog, A.; Visscher, P. T. *Mar. Chem.* submitted for publication.
(55) Lindberg, S. E.; Harriss, R. C. *Environ. Sci. Technol.* **1974**, *5*, 459−462.
(56) Westrich, J. T.; Berner, R. A. *Limnol. Oceanogr.* **1984**, *29*, 236−249.
(57) Berner, R. A.; Westrich, J. T. *Am. J. Sci.* **1985**, *285*, 193−206.
(58) Goldhaber, M. B.; Aller, R. C.; Cochran, J. K.; Rosenfeld, J. K.; Martens, C. S.; Berner, R. A. *Am. J. Sci.* **1977**, *277*, 193−237.
(59) Hines, M. E.; Jones, G. E. *Estuar. Coast. Shelf Sci.* **1985**, *20*, 729−742.
(60) Skyring, G. W. *Geomicrobiol. J.* **1987**, *5*, 295−374.
(61) Wright D. R.; Hamilton, R. D. *Can. J. Fish. Aquat. Sci.* **1982**, *39*, 1459−1466.
(62) Roden, E. E.; Zachara, J. M. *Environ. Sci. Technol.* **1996**, *30*, 1618−1628.
(63) Fredrickson, J. K.; Zachara, J. M.; Kennedy, D. W.; Dong, H.; Onstott, T. C.; Hinman, N. W.; Li, S.-M. *Geochim. Cosmochim. Acta* **1998**, *62*, 3239−3257.
(64) Glauser, S.; Weidler, P. G.; Langley, S.; Beveridge, T. J. *Geochim. Cosmochim. Acta* **2003**, *67*, 1277−1288.
(65) Mehrotra, A. S.; Horne, A. J.; Sedlak, D. L. *Environ. Sci. Technol.* **2003**, *37*, 3018−3023.
(66) Kelly, C. A.; Rudd, J. W. M.; Holoka, M. H. *Environ. Sci. Technol.* **2003**, *37*, 2941−2946.
(67) Capone, D. J.; Kiene, R. P. *Limnol. Oceanogr.* **1988**, *33*, 725−745.
(68) King, J. K.; Kostka, J. E.; Frischer, M. E.; Saunders, F. M. *Appl. Environ. Microbiol.* **2000**, *66*, 2430−2437.
(69) King, J. K.; Saunders, F. M.; Lee, R. F.; Jahnke, R. A. *Environ. Toxicol. Chem.* **1999**, *18*, 1362−1369.
(70) Jorgensen, B. B. *Limnol. Oceanogr.* **1977**, *22*, 814−832.
(71) Gagnon, C.; Mucci, A.; Pelletier, É. *Mar. Chem.* **1996**, *52*, 195−209.
(72) Hammerschmidt, C. R.; Fitzgerald, W. F.; Lamborg, C. H.; Balcom, P. H.; Visscher, P. T. *Mar. Chem.*, submitted for publication.

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